

ALIEN PROPERTY CUSTODIAN

RESIN-LIKE RUBBER CONVERSION PRODUCTS

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This invention relates to the production of isomerization products of rubber and rubber-like products whereby rubber conversion products are obtained having resinous properties, such products being suitable for many uses throughout the arts.

A process has heretofore been formulated for the conversion of rubber into resin-like products by subjecting rubber to the action of phenols and acids which do not form compounds with phenols, or salts capable of inducing isomerization, such process being carried out by heating unvulcanized or vulcanized rubber while in admixture with one or more phenolic compounds and with the isomerizing agent or catalytic agent for a relatively short reaction period at a temperature up to, but not higher than, the boiling point of the phenolic component present.

An object of the present invention is to improve upon this process by increasing its efficiency and by improving the properties of the resin-like conversion product obtained.

In accordance with the process of the present invention, the conversion of the rubber compound through the action of the phenolic agent and the isomerizing agent is effected at temperatures higher than the boiling point of the phenolic agent employed. In order to carry out the conversion process at such temperatures, the process is effected in an autoclave wherein a superatmospheric pressure exists. The use of superatmospheric pressure also serves to assist the conduct of the reaction.

Through the use of the process of the present invention, the reaction time is lessened to a considerable degree and the amount of isomerizing agent or catalyst required is reduced to a substantial degree. The conversion reaction which brings about the isomerization of the rubber material treated, forming the resin-like rubber product, is aided by the increased reaction temperature and also by the consequent shorter reaction period required, for side reactions serving no useful purpose, and resulting from the longer reaction period as heretofore employed, are strongly repressed or are practically prevented from occurring. Through the use of the instant process, it is possible to obtain a very homogeneous final product having improved or superior properties.

In accordance with an important embodiment of the present invention, the conversion reaction is carried out in the substantial absence of water. Unless special effort is made to operate in the absence of water, such compound will be unavoidably brought into the reaction mass in the

various raw materials employed, including the phenols or the rubber or the isomerizing agent. It has now been discovered that the presence of water in many instances has a decided detrimental effect upon the process. The water may be removed from the raw materials in any one of a number of ways, but in accordance with a very satisfactory method, constituting a feature of one embodiment of the invention, an excess of phenol is introduced into the initial mixture before the start of the actual conversion and the mixture subjected to distillation to remove its water together with the excess of phenol, after which the heating is continued to bring about the isomerizing reaction. The removal of water in this manner is of advantage to the isomerizing process whether the conversion be effected below or at the boiling point of the phenolic component or at a temperature above the boiling point with operation under superatmospheric pressure.

In accordance with another embodiment of the present invention, the isomerizing reaction is carried out in the substantial absence of oxygen. It has been discovered that the presence of oxygen or other oxidizing agents have a depolymerizing and decomposing effect upon the rubber treated or the rubber product formed, and now also that the influence of any oxygen present is detrimental to the instant isomerizing reaction of the process of the instant invention. This discovery indicates that the instant conversion process is quite different from the decomposition of rubber due to the catalytic effect of oxygen. The oxygen is preferably removed from the reaction mixture by passing an inert gas, such as carbon dioxide, nitrogen or the like therethrough. This treatment improves the conversion reaction and decreases the time required for the reaction. It is therefore advantageous to operate the instant process in the presence of an inert gas after the removal of oxygen, the advantages being obtained whether the conversion be effected under normal pressures or under raised pressures.

The instant process is not only applicable to the treatment of natural rubber and vulcanized products thereof, but is also suitable for the treatment of synthetic rubber or rubber-like compounds prepared from polymerized hydrocarbons, as for example, the product known as Buna. Other raw materials include Neoprene, and Duprene. Isomerizing agents or catalysts found to give excellent results comprise borohalide compounds or the halogen derivatives of boron, such as borofluoride, and also compounds

thereof, such as borofluoride acetic acid. These catalysts are preferred not only because of their effectiveness in causing the reaction to proceed but also because of their fluid nature, which permits them to be easily removed from the reaction mixture.

The purification of the reaction mass to separate the phenolic reaction medium and the catalyst from the resin-like reaction product may be effected in several ways. In accordance with one method, the phenolic material is removed by direct distillation, preferably with the aid of a vacuum and with agitation. The distillation may also be carried out with the aid of steam. Further separation may be brought about by the action of mechanical working devices, such, for example, as rollers or kneaders.

In accordance with another method, the undesired materials may be separated by grinding the reaction mass in a ball mill in the presence of a solvent for the phenolic material, such for example, as a solution of an alkali metal hydroxide or an alcohol. Then the reaction mass in the dissolved state may be extracted by a treatment with those substances which dissolve the phenolic component or the catalyst or both of such components, suitable solvents being solutions of caustic soda. Alternatively, such solutions may be distilled over with the aid of other volatile substances which assist in the evaporation of the phenolic component.

In accordance with other processes for purification, solutions of the reaction mass may be treated with liquid materials that dissolve the phenolic component but which do not dissolve the rubber conversion product. In working with substances which do not dissolve the rubber reaction product, the direct application of such solvents has been found quite effective. Substances suitable for such treatment are those containing alcoholic groups, but which have little or no solvent power for the rubber substances at normal temperatures, or those which have the power to dissolve such substances only at elevated temperatures. Under this procedure, it is possible to wash out the phenolic component and the catalyst by using alcohols, the boiling points of which are above the softening point of the resin component, examples of the alcohols being butyl alcohol, amyl alcohol, hexyl alcohol or cyclohexanol, which are mixed with the resin product with the aid of heat and of stirring, kneading or trituration.

In accordance with another but important embodiment, the separation is effected through the use of substances possessing boiling points below the softening point of the resin product. When these substances are used, it is necessary to work under superatmospheric pressure. The resin-like product treated in this manner can be freed of the phenolic component much more easily, since the mass is in the form of a liquid permitting more intimate contact with the washing medium.

The resin-like rubber products produced in accordance with the instant invention, depending upon the conditions under which they are produced, may be obtained in granulated form, in the form of a powder, or, after being melted, in the form of a resin. The resin-like product may be used in industrial applications as such, or it may be combined with any number of various substances. For example, they may be added to various oils and lacquers, or, such binding agents may be added to them. The resin-like products may be compounded advantageously with natural resins or with synthetic resins, especially with

alkyd resins, other rubber products or caoutchouc derivatives such as the halogen-caoutchouc or with bitumen, pitch, wax, cellulose derivatives, fillers, dye stuffs, lubricants and other compounds.

The resin-like products may be applied in undiluted form, in solution or in emulsified form. Such products may be used to produce protective coatings or finishing coatings to materials of many kinds, including threads, wires, ropes, bands, films and foils. They may also be used as adhesives, as adhesive layers, as sizing or finishing materials for textiles, as impregnation materials, as binding agents for layers of materials and as pressing and spraying materials.

In the following illustrative examples, all parts are given by weight.

Example 1

2.5 parts of rubber, through which carbon dioxide has been passed is introduced into a stirring autoclave together with a mixture of 5 parts of phenol and 0.2 parts of orthophosphoric acid through which nitrogen has been led when in a fluid state. After causing the reaction mixture to liquefy at ordinary pressure and feeding carbon dioxide therethrough, 0.5 parts of phenol is distilled therefrom. This distillation treatment removes the water content of the reaction mixture. The autoclave is then closed and the temperature raised to 210° C. With good stirring the conversion of the rubber will have taken place within 1 to 2 hours. The reaction mass, from which a part of the phenol and a greater part of phosphoric acid will have settled to the bottom, is removed from the reaction container by the use of pressure. The raw product of the conversion reaction, which is a solid solution of phenol and rubber conversion product in substantially equal proportions, is heated in twice its volume of ethyl alcohol in a pressure container to about 140° C. and thoroughly stirred. The phenol-alcohol mixture is then separated from the rubber resin, and the extracting is repeated about 4 to 5 times, or until the phenol content of the rubber resin is less than 0.2%.

The phenol- and acid-free alcohol containing conversion product is ground in a closed mill and dried. In its powdered form it is a coarse, almost white powder.

Example 2

1 part of Buna 85 after being cut into small pieces is added to 5 parts of a cresol mixture (meta and para) to which 0.05 parts of borofluoride acetic acid have been added and the mixture is heated in a closed container to 200° C. while being stirred. After several hours, the conversion of the rubber is sufficiently complete and the cresol solution present is worked with alcohol until no further precipitate results. The precipitated rubber substance is then dissolved in twice its volume of toluol and is again precipitated with alcohol. A phenol-free product is obtained by successively dissolving and precipitating four times. This product is freed from the absorbed and occluded alcohol by spraying it in an evacuated chamber, the final product being obtained in a finely divided form.

The production of resin-like products by the action of phenols and catalytic agents at temperatures up to the boiling point of the phenolic component is described in the earlier co-pending application, Serial No. 147,479, filed June 10, 1937.

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